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**(54) [Title of the Invention]****Heat-shrinkable Polyester Film****(57) [Claims]**

**[Claim 1]** A heat-shrinkable polyester film formed from a composition comprising 100 parts by weight of a polyester resin derived from a dicarboxylic acid component and a diol component, and 1 to 40 parts by weight of at least one plasticizer selected from those based on phthalic acid ester, polyester, aliphatic dibasic acid ester, aliphatic monobasic acid ester, phosphoric acid ester, citric acid ester, epoxy, trimellitic acid ester, tetrahydrophthalic acid ester, glycol, and bisphenol A alkylene oxide derivatives.

## **[Detailed Description of the Invention]**

### **[Technological Field of the Invention]**

The present invention relates to a heat-shrinkable polyester film, and more specifically relates to a heat-shrinkable polyester film that has excellent low-temperature shrinkage, uniform shrinkage, and other features, and is particularly useful as a shrink label for containers.

### **[Prior Art]**

The ability of heat-shrinkable films to be shrunk by reheating is widely used in shrink wrapping, shrink labeling, cap seals, and other applications.

Vinyl chloride resin, and polystyrene foam and other uniaxially oriented films are mainly used as the shrinkable label on polyethylene terephthalate (PET) containers, glass containers, and other types of containers. Among these, heat-shrinkable vinyl chloride film is commonly used for its good heat-shrinking properties and printing characteristics.

Vinyl chloride resin has drawbacks in that its heat resistance is low, and hydrogen chloride is generated when the resin is burned. The containers that have used heat-shrinkable vinyl chloride film as a shrink label have a drawback in that the PET container cannot be recycled together with the shrink label.

Since heat-shrinkable films composed of polyethylene terephthalate or another polyester resin have excellent heat resistance, do not generate hydrogen chloride when burned, and have other characteristics not possessed by vinyl chloride resin, there are expectations for their use as shrink labels for containers in place of heat-shrinkable films composed of vinyl chloride resin.

However, since polyester resin has high crystallinity, the heat-shrinkage start temperature is relatively high in a heat-shrinkable film composed thereof, the shrinkage factor tends to rapidly increase together with the rise in temperature, and there are drawbacks from the aspects of productivity and uniform shrinkage in shrink label applications for containers.

In view of the above, various proposals have recently been made for improving heat-shrinkable films composed of polyester resin.

Proposed in JP (Kokai) 57-42726 is a heat-shrinkable wrapping film that is transparent and has heat sealing properties obtained by using a copolyester composed of terephthalic acid as a dicarboxylic acid component, and ethylene glycol and 1,4-dicyclohexane dimethanol as diol components.

JP (Kokoku) 63-7573 proposes to alleviate high crystallinity and to improve nonuniform shrinkage and heat sealing properties by including isophthalic acid as a copolymerizing component.

Proposed in JP (Kokoku) 64-10332 is a highly shrinkable polyester film in which a composition composed of a noncrystalline copolyester derived from tetrathalic acid or a derivative thereof, ethylene glycol, and 1,4-dicyclohexane dimethanol, and a polyester polymer composed of ethylene glycol and terephthalic acid or a derivative thereof is formed into a film by drawing.

In the foregoing references, a noncrystalline copolyester, or a copolyester in which the crystallinity of the polyester is inhibited by admixing a noncrystalline copolyester and a crystalline polyester are used as the raw material of a heat-shrinkable polyester film. In comparison with a heat-shrinkable film in which a crystalline polyester terephthalate is used as the raw material, the shrinkage is considerable, the heat sealing strength is greater, the stress from the shrinkage force is reduced, and nonuniform shrinking and the tendency to tear along the heat sealing portions are improved.

However, a heat-shrinkable polyester film with adequate shrinking properties is not obtained in the above-described prior arts.

More specifically, the above-described known heat-shrinkable polyester films, in comparison with heat-shrinkable vinyl chloride films, have drawbacks in that they still have a high shrinking temperature, and the shrinkage factor rapidly increases at the shrinkage start temperature.

For this reason, problems such as reduced productivity in the shrinking step and the occurrence of nonuniform shrinking cannot be avoided. In the particular case in which such film is used as a shrink label for bottles and other containers with different sizes in the neck and body portions, the rapid increase in shrinkage that is associated with the temperature increase creates nonuniform adhesion and warped printing, resulting in significant drawbacks in practical terms.

#### **[Problems Which the Invention Is Intended to Solve]**

An object of the present invention is to provide a heat-shrinkable polyester film that has a good shrinkage factor at low temperatures and that can achieve a completely uniform shrinkage.

As a result of thoroughgoing research aimed at overcoming the drawbacks in the prior art described above, the present inventors discovered that a heat-shrinkable polyester film formed

using a composition obtained by admixing plasticizers based on phthalic acid ester, polyester, aliphatic dibasic acid ester, aliphatic monobasic acid ester, phosphoric acid ester, citric acid ester, epoxy, trimellitic acid ester, tetrahydrophthalic acid ester, glycol, bisphenol A alkylene oxide derivatives, and the like into a polyester resin derived from a dicarboxylic acid component and a diol component is capable of reducing the shrinking temperature to the level of a heat-shrinkable vinyl chloride film and achieving completely uniform shrinkage because shrinkage gradually increases as the temperature of the film increases.

The present invention was perfected on the basis of these findings.

#### **[Means Used to Solve the Above-Mentioned Problems]**

The present invention provides a heat-shrinkable polyester film formed from a composition comprising 100 parts by weight of a polyester resin derived from a dicarboxylic acid component and a diol component, and 1 to 40 parts by weight of at least one plasticizer selected from those based on phthalic acid ester, polyester, aliphatic dibasic acid ester, aliphatic monobasic acid ester, phosphoric acid ester, citric acid ester, epoxy, trimellitic acid ester, tetrahydrophthalic acid ester, glycol, and bisphenol A alkylene oxide derivatives.

The present invention is described in detail below.

#### **(Polyester resin)**

The polyester resin used in the present invention is a polyester resin derived from a dicarboxylic acid component and a diol component, or a polyester resin derived from an oxycarboxylic acid component, or a mixture thereof. Examples of the dicarboxylic acid component include terephthalic acid, isophthalic acid, phthalic acid, naphthalene dicarboxylic acid, diphenylene dicarboxylic acid, diphenyl ether dicarboxylic acid, phenylene diacetic acid, adipic acid, azelaic acid, sebacic acid, oxalic acid, succinic acid, malonic acid, glutaric acid, pimelic acid, suberic acid, dodecadienoic acid, cyclohexane dicarboxylic acid, and carbonic acid. Examples of the diol component include ethylene glycol, propylene glycol, neopentyl glycol, butanediol, hexanediol, 1,4-cyclohexane dimethanol, diethylene glycol, polyalkylene glycol, xylene glycol, hydroquinone, resorcinol, dihydroxy diphenyl, and alkylene oxide adducts of bisphenol A. Examples of the oxycarboxylic acid component include oxybenzoic acid, oxyalkyl benzoic acid, oxyalcoxyphenyl acetic acid, oxynaphthoic acid, and glycolic acid.

Particularly advantageous among these are those obtained using polyester resin in which terephthalic acid comprises 50 mol% or more of the dicarboxylic acid component and in which ethylene glycol comprises 50 mol% or more of the diol component, because crystallization is easily inhibited and the heat sealing properties are excellent.

The plasticizer used in the present invention is at least one selected from the plasticizers described above, but more specific examples are provided below.

Examples of the phthalic acid ester plasticizer include dibutyl phthalate, dioctyl phthalate, diheptyl phthalate, and other phthalic acid dialkyl esters, as well as dibenzyl phthalate.

Examples of the polyester plasticizer include ethylene glycol, propylene glycol, 1,3-butanediol, 1,6-hexanediol, and copolymers of adipic acid, sebacic acid, and phthalic acid.

Examples of the aliphatic dibasic acid ester plasticizer include dioctyl adipate, diisodecyl adipate, dioctyl azelate, dihexyl azelate, dioctyl sebacate, and diisooctyl sebacate.

Examples of the aliphatic monobasic acid ester plasticizer include butyl stearate, amyl stearate, and butyl oleate.

Examples of the phosphoric acid ester plasticizer include trioctyl phosphate, triphenyl phosphate, and 2-ethylhexyl diphenyl phosphate.

Examples of the citric acid ester plasticizer include tributyl citrate, tributyl acetylcitrate, and tri-2-ethylhexyl acetylcitrate.

Examples of the epoxy plasticizer include epoxidated soybean oil, epoxidated linseed oil, and octyl epoxy stearate.

Examples of the trimellitic acid ester plasticizer include tributyl trimellitate, trihexyl trimellitate, and trioctyl trimellitate.

Examples of the tetrahydrophthalic acid ester plasticizer include dioctyl tetrahydrophthalate and diisodecyl tetrahydrophthalate.

Examples of the glycol plasticizer include polyethylene glycol and polyethylene glycol benzoate.

Examples of the bisphenol A alkylene oxide derivative plasticizer include compounds in which ethylene oxide or propylene oxide has been added to bisphenol A.

These plasticizers may be used alone, or in a combination of two or more.

(Blend ratio)

The blend ratio of the polyester resin and the plasticizer in the present invention is 1 to 40 parts by weight of the plasticizer per 100 parts by weight of the polyester resin, is preferably 2 to 30 parts by weight, and is more preferably 3 to 15 parts by weight.

Adding a plasticizer inhibits the crystallization of the polyester resin and allows molecular chains to slide more easily in relation to each other, and when the product is used as a heat-shrinkable film, shrinking can be started gradually from a low temperature. When the blend ratio of the plasticizer is less than 1 part by weight, adequate intermolecular chain sliding does not occur and low-temperature shrinking is inadequate, and when the blend ratio is conversely greater than 40 parts by weight, the elasticity of the film at the drawing temperature during production of the heat-shrinkable film is markedly reduced and drawing becomes difficult, and a heat-shrinkable film cannot be obtained.

It should be noted that in the composition in the present invention, fillers, coloring agents, and other additives may be added as desired.

(Heat-shrinkable film production)

An undrawn film is obtained using ordinary methods by melt extruding the resin composition composed of a polyester resin and a plasticizer into the form of a sheet using the T-die method, tubular method, or another method. Next, the undrawn film is drawn about 150% to 600% in at least one axial direction by the roll, tenter, or tubular method, or by another method to obtain a heat-shrinkable polyester film.

#### **[Operation of the Invention]**

The heat-shrinkable polyester film obtained by adding a specific plasticizer as described above has low-temperature shrinkage at about 70°C, which is substantially the same as a heat-shrinkable vinyl chloride film.

Heat-shrinkage additionally tends to increase gradually as the temperature increases from the heat-shrinkage start temperature.

Therefore, when the heat-shrinkable polyester film is used as a shrink label for containers, such as bottles with a narrow portion such as the neck and a broad portion such as the body, shrinkage is uniform, adhesion is good, and print warping does not occur because the shrinkage

gradually increases, even if a cylindrical label for shrinking is applied to the narrow and broad locations.

Since the heat-shrinkable polyester film has superior heat resistance in comparison with vinyl chloride resin, it can be used as a shrink film for PET containers, for example, and the label does not deform even under retorting.

Hydrogen chloride is not generated during burning as vinyl chloride resin does. Since the heat-shrinkable polyester film is composed of the same raw material as a PET container, the PET resin can be recovered and reused with the label left attached to the bottle.

Thus, in comparison with a conventional heat-shrinkable polyester film, productivity is improved because shrinking starts at a low temperature, nonuniformity does not occur because the shrinkage gradually increases as the temperature of the film increases, and other excellent shrinking characteristics are demonstrated.

#### **[Working Examples]**

The present invention is concretely described below with working and comparative examples.

It should be noted that "parts by weight" is simply written as "parts."

#### **(Working example 1)**

A composition composed of 100 parts copolyester composed of terephthalic acid as the dicarboxylic acid component, and 70-mol% ethylene glycol and 30-mol% 1,4-cyclohexane dimethanol as the diol component; and 5 parts of dibutyl phthalate (DBP) as the plasticizer was melt extruded to obtain an undrawn film with a thickness of 120  $\mu\text{m}$ .

The undrawn film was drawn 300% in the transverse direction at 80°C to obtain a heat-shrinkable film with a thickness of 40  $\mu\text{m}$ .

The heat-shrinkable film was measured for shrinkage in the transverse direction at 10°C intervals in a temperature range of 60°C to 110°C.

Measurement of the shrinkage was carried out by cutting a sample 100 mm in the transverse direction and 10 mm in the width direction, and shrinking the sample for five minutes in hot air set to the measurement temperature.



**(Working examples 2 to 19)**

Other than using the compositions composed of 100 parts polyester resin and 5 parts plasticizer, as shown in Table 1, heat-shrinkable films were obtained in the same manner as described in working example 1, and the same evaluations were carried out.

**(Comparative examples 1 and 2)**

Other than using the polyester resins shown in Table 1 and avoiding the use of a plasticizer, heat-shrinkable films were obtained in the same manner as described in working example 1, and the same evaluations were carried out.

The results of working examples 1 to 19 and comparative examples 1 and 2 are collectively shown in Table 2.

**Table 1 (Part 1)**

		Polyester resin (numbers in parentheses are mol%)		Plasticizer
		Dicarboxylic acid	Diol	
Working Example	1	Terephthalic acid	Ethylene glycol (70) 1,4-dicyclohexane dimethanol (30)	Diethyl phthalate (DBP)
	2	Terephthalic acid (90) Isophthalic acid (10)	Ethylene glycol	Diethyl phthalate (DOP)
	3	Polyethylene terephthalate		Diethyl phthalate (DHP)
	4	Terephthalic acid	Ethylene glycol (70) 1,4-dicyclohexyl dimethanol (30)	Phthalic acid polyester (Polycizer P-29 *1)
	5	Terephthalic acid (90) Isophthalic acid (10)	Ethylene glycol	Adipic acid polyester (Polycizer W-4000 *2)
	6	Polyethylene terephthalate		Sebacic acid polyester (Polycizer P-202 *3)
	7	Terephthalic acid	Ethylene glycol (70) 1,4-dicyclohexyl dimethanol (30)	Diethyl sebacate (DOS)
	8	Terephthalic acid (90) Isophthalic acid (10)	Ethylene glycol	Diethyl azelate (DOZ)
	9	Polyethylene terephthalate		Diethyl Adipate (DOA)

\*1, \*2, \*3: Manufactured by Dainippon Ink and Chemicals

**Table 1 (Part 2)**

		Polyester resin (numbers in parentheses are mol%)		Plasticizer
		Dicarboxylic acid	Diol	
Working Example	10	Terephthalic acid	Ethylene glycol (70) 1,4-dicyclohexane dimethanol (30)	Butyl oleate (BO)
	11	Terephthalic acid (90) Isophthalic acid (10)	Ethylene glycol	Butyl stearate (BS)
	12	Terephthalic acid	Ethylene glycol (70) 1,4-dicyclohexyl dimethanol (30)	2-Ethylhexyl diphenyl phosphate (ODP)
	13	Terephthalic acid (90) Isophthalic acid (10)	Ethylene glycol	Trioctyl phosphate (TOP)
	14	Terephthalic acid	Ethylene glycol (70) 1,4-dicyclohexyl dimethanol (30)	Tributyl acetyl citrate (ATBC)
	15	Terephthalic acid (90) Isophthalic acid (10)	Ethylene glycol	Tributyl citrate (TBC)
	16	Terephthalic acid	Ethylene glycol (70) 1,4-dicyclohexyl dimethanol (30)	Epoxidated soybean oil (ESBO)
	17	Terephthalic acid	Ethylene glycol (70) 1,4-dicyclohexyl dimethanol (30)	Trioctyl trimellitate (TOTM)
	18	Terephthalic acid	Ethylene glycol (70) 1,4-dicyclohexyl dimethanol (30)	Dioctyl tetrahydrophthalate (DOTP)

**Table 1 (Part 3)**

		Polyester resin (numbers in parentheses are mol%)		Plasticizer
		Dicarboxylic acid	Diol	
Working Example	19	Terephthalic acid	Ethylene glycol (70) 1,4-dicyclohexane dimethanol (30)	Dioctyl phthalate (DBP)
	20	Terephthalic acid	Ethylene glycol (70) 1,4-dicyclohexyl dimethanol (30)	Dioctyl phthalate (DOP)
Comparative Example	1	Terephthalic acid	Ethylene glycol (70) 1,4-dicyclohexyl dimethanol (30)	—
	2	Terephthalic acid (90) Isophthalic acid (10)	Ethylene glycol	—

\*4: Manufactured by Sanyo Chemical Industries

**Table 2 (Part 1)**

		Heat shrinkage (transverse direction %)					
		60°C	70°C	80°C	90°C	100°C	110°C
Working example	1	5	38	52	60	67	70
	2	3	23	46	58	60	60
	3	0	18	45	52	50	50
	4	3	40	51	58	63	65
	5	4	43	56	64	68	69

**Table 2 (Part 2)**

		Heat shrinkage (transverse direction %)					
		60°C	70°C	80°C	90°C	100°C	110°C
Working example	6	0	23	43	50	53	54
	7	6	40	62	64	62	62
	8	2	24	62	64	63	53
	9	0	15	48	56	51	50
	10	5	41	64	65	65	65
	11	0	17	56	64	64	65
	12	5	45	66	66	66	68
	13	3	38	60	65	64	65
	14	8	46	56	61	64	67
	15	4	38	66	67	68	67
	16	0	16	57	60	59	59
	17	2	21	63	66	66	66
	18	6	42	65	65	66	66
	19	0	10	58	60	60	59
	20	0	30	65	65	66	65
Comparative example	1	0	2	63	65	68	68
	2	0	3	40	39	38	36

It is apparent from Table 2 that the heat-shrinkable polyester film of the present invention can shrink at low temperatures in the vicinity of 70°C, which is the heat-shrinkage start temperature of heat-shrinking vinyl chloride film. Another important feature is that shrinkage tends to gradually increase as the shrinking temperature rises. The phenomenon whereby nonuniform shrinking occurs due to a rapid increase in the shrinkage can therefore be overcome.

In contrast, the heat-shrinkable polyester film of comparative examples 1 and 2, in which a plasticizer was not used, exhibited a rapid increase in the shrinkage at the heat-shrinkage start temperature of 80°C.

#### **[Effect of the Invention]**

In accordance with the present invention, a heat-shrinkable polyester film that can shrink at low temperatures and has excellent, completely uniform shrinking properties can be provided.

The heat-shrinking polyester film of the present invention has good heat resistance and does not generate hydrogen chloride when burned, as vinyl chloride resin does. Since shrinkage does not rapidly increase as the shrinking temperature rises, but rather increases gradually to allow completely uniform shrinking to be achieved, the film is useful in the field of shrink labels for PET containers and other containers.

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